



Europäisches Patentamt
European Patent Office
Office européen des brevets

Publication number:

**0 385 734
A2**

EUROPEAN PATENT APPLICATION

Application number: 90302092.3

Int. Cl.⁵ C08F 218/08, C09J 131/04

Date of filing: 27.02.90

Priority: 28.02.89 JP 49565/89
13.12.89 JP 324797/89

Date of publication of application:
05.09.90 Bulletin 90/36

Designated Contracting States:
DE GB IT

Applicant: SUMITOMO CHEMICAL COMPANY,
LIMITED
5-33 Kitahama 4-chome Chuo-ku
Osaka-shi Osaka(JP)

Inventor: Oyamada, Takeo
1-9, Yushudainishi
Ichihara-shi, Chiba(JP)
Inventor: Taira, Yoshito
832-4, Shizu

Ichihara-shi, Chiba(JP)
Inventor: Nitta, Masayoshi
311-9, Takinoguchi, Sodegauramachi
Kimitsu-gun, Chiba(JP)
Inventor: Kaneshima, Yasuo
1-9, Yushudainishi
Ichihara-shi, Chiba(JP)
Inventor: Kurino, Tateshi
1-9 Yushudainishi
Ichihara-shi, Chiba(JP)
Inventor: Narisawa, Shizuo
3-21-5 Aobadai
Ichihara-shi, Chiba(JP)

Representative: Diamond, Bryan Clive et al
Gee & Co., Chancery House, Chancery Lane
London WC2A 1QU(GB)

Adhesive composition containing a vinyl acetate ethylene copolymer and production thereof by polymerisation.

A dispersant is prepared by mixing in water by weight (i) 1.0 to 1.9 parts of polyvinyl alcohol saponified to less than 96% (preferably at least 70%) with (ii) 1.0 to 3.0 parts of a polyoxyethylene non-ionic surfactant, of HLB 16.5 to 17.5 to make a solution (D) containing 2.5 to less than 5.0 parts of dispersant; and a reducing agent part of a redox catalyst;

40 to 90% of 100 parts of the vinyl acetate (VA) to be polymerized is added to (D) and stirred to make a dispersion stable for at least 10 hours, and a polymerization is performed by subjecting the dispersion to ethylene at pressure of 98 - 980 Pa at 30 - 80 °C and adding the remaining 10 to 60% of the VA and an oxidizing agent part of the catalyst; optionally up to 30% of the dispersant (D) is added in this step.

A third monomer having a functional group may be copolymerized in amount of 10 to 100 parts by weight of the VA.

There is obtained an aqueous dispersion ("emulsion") of particles of not larger than 0.9µm of

a copolymer of ethylene and vinyl acetate together with said dispersant; the dispersion has a good properties as an adhesive on a variety of substrates.

EP 0 385 734 A2

ADHESIVE COMPOSITION CONTAINING A VINYL ACETATE ETHYLENE COPOLYMER AND PRODUCTION THEREOF BY POLYMERISATION

This invention relates to a vinyl acetate-ethylene copolymer emulsion, which is capable of providing an adhesive having good properties as regards its initial adhesion, resistance to thermal creep, low-temperature adhesion, dry strength and wet strength, resistance to water retention, and resistance to water blushing and being adhesive to a wide variety of surfaces.

The invention also relates to a process for the industrial production of the aforementioned vinyl acetate-ethylene copolymer emulsion, whereby little scum is formed and the emulsion has a suitable viscosity.

Various properties have been required for adhesives and recently, with the increase in the variety of objects to be adhered and the use of high-speed adhering machines, adhesives have been desired which are suitable for the adhesion of a wide range of materials, quickly develop adhesion power after adhesion, and are excellent in the so-called initial adhesion properties.

As an adhesive meeting such requirements, a vinyl acetate-ethylene copolymer emulsion having a high solids content is known.

For example, a vinyl acetate-ethylene copolymer emulsion having a solids content of from 45 to 60% by weight is described in JP-B-52-34650 (the term "JP-B" as used herein means an "examined Japanese patent publication"). Also, JP-B-42-22692 describes a process of producing a vinyl acetate-ethylene copolymer emulsion having a solids content of up to 70% by weight by using a polyoxyethylene-polyoxypropylene block copolymer as a surface active agent. Furthermore, JP-B-43-17538 describes a process of obtaining a vinyl acetate-ethylene copolymer emulsion having a solids content of from 60 to 70% by weight by using a surface active agent having an HLB (hydrophilic-lipophilic balance) of from 3 to 8 as an emulsifying dispersant before the polymerization reaction and adding a surface active agent having an HLB of at least 8 during the polymerization.

Furthermore, JP-A-60-1272 describes a polyvinyl acetate or vinyl acetate-ethylene copolymer emulsion having a solids content of from 55 to 70% by weight using specific polyvinyl alcohol of a low polymerization degree having an average polymerization degree of from 20 to 300 and having modified polymer terminals as an emulsifying dispersant. (The term "JP-A" as used herein means an "unexamined published Japanese patent application"). Moreover, JP-A-63-223053 describes a vinyl acetate-ethylene copolymer emulsion having a solids content of from 65 to 70% by weight and a

viscosity of not higher than 3,500 cps at a solids content of 65% by weight by adding polyvinyl alcohol and a surface active agent in amounts of from 2 to 4% by weight and from 1 to 4% by weight, respectively to a vinyl acetate monomer as emulsifying dispersants.

On the other hand, with the increase of the wide use of hydrophobic materials such as plastics, water-repellent papers and resin-coated papers, as materials to be adhered using adhesives and with the development of increased high-speed adhering machines, the requirement for increasing the speed showing the adhesion power of adhesives, that is, the requirement for the initial adhesion properties of adhesives has been further enhanced. Furthermore, adhesives have recently been required to be suitably used for adhering various kinds of materials including the aforementioned hydrophobic materials and to give a high adhesion strength under various conditions. Also, it is, as a matter of course, necessary that such adhesives can be produced industrially without difficulty.

Adhesives meeting the aforesaid requirements are not yet known; an object of this invention is thus to provide a vinyl acetate-ethylene copolymer emulsion capable of adequately meeting the aforesaid requirements as an adhesive.

A further object of this invention is to provide a vinyl acetate-ethylene copolymer emulsion which forms a dry film without the occurrence of a blushing phenomenon when the film is brought into contact with water; it is an important factor for adhesives to avoid such a blushing phenomenon. The technique described in the above-cited JP-A-63223053 is, however, inadequate for this purpose.

Another object of this invention is to provide a process for producing the aforesaid vinyl acetate-ethylene copolymer emulsion.

According to one embodiment of this invention there is provided a copolymer emulsion comprising (i) a copolymer of vinyl acetate and ethylene composed of from 10 to 40% by weight of an ethylene unit and from 90 to 60% by weight of a vinyl acetate unit and (ii) an emulsifying dispersant in an amount by weight of from 2.5 parts or more but less than 5.0 parts per 100 parts of the vinyl acetate unit, and having a mean particle size of not larger than 0.9 μm and a solids content of from 65 to 75% by weight, wherein the emulsifying dispersant contains by weight, (a) from 1.0 to 1.9 parts of partially saponified polyvinyl alcohol prepared so as to have an average polymerization degree of from 300 to 1,000 and (b) from 1.0 to 3.0 parts of a polyoxyethylene nonionic surface active agent hav-

ing an HLB of from 16.5 to 17.5, per 100 parts of the vinyl acetate unit.

We also provide a process for producing the aforesaid vinyl acetate-ethylene copolymer emulsion, comprising a first step of mixing with stirring from 1.0 to 1.9 parts by weight of partially saponified polyvinyl alcohol prepared so as to have an average polymerization degree of from 300 to 1,000 and from 1.0 to 3.0 parts by weight of a polyoxyethylene nonionic surface active agent having an HLB of from 16.5 to 17.5 per 100 parts by weight of the whole of vinyl acetate to be polymerized together with a reducing agent of a redox catalyst, water, and, if desired, a pH buffer to provide an aqueous solution containing 2.5 parts by weight or more but less than 5.0 parts by weight of the emulsifying dispersant per 100 parts by weight of the vinyl acetate; a second step of adding from 40 to 90% by weight of vinyl acetate to be polymerized to the aqueous solution of the emulsifying dispersant under stirring to provide a stable vinyl acetate emulsified dispersion; and a third step of carrying out a polymerization reaction at a polymerization temperature of from 30 to 80 °C and an ethylene pressure of from 98-980 Pa (10 to 100 kg/cm²) by using the vinyl acetate emulsified dispersion, while successively adding from 10 to 60% of vinyl acetate which is the residue of vinyl acetate to be polymerized to the polymerization system during the polymerization and further adding thereto at least 0.004 mole of an oxidizing agent of a redox catalyst per kilogram of the whole vinyl acetate supplied within 3 hours after the initiation of the polymerization.

The vinyl acetate-ethylene copolymer emulsion of this invention contains a vinyl acetate-ethylene copolymer and an emulsifying dispersant as main components.

The vinyl acetate-ethylene copolymer is composed of from 10 to 40% by weight of an ethylene unit and from 90 to 60% by weight of a vinyl acetate unit.

The emulsifying dispersant is contained in the vinyl acetate-ethylene copolymer emulsion of this invention in the range of 2.5 parts by weight or more but less than 5.0 parts by weight per 100 parts by weight of the vinyl acetate unit constituting the vinyl acetate-ethylene copolymer. Also, the emulsifying dispersant contains partially saponified polyvinyl alcohol and a polyoxyethylene nonionic surface active agent as main components.

The partially saponified polyvinyl alcohol for use in this invention as one main component of the emulsifying dispersant is partially saponified polyvinyl alcohol prepared so as to have an average polymerization degree of from 300 to 1,000, and preferably from 400 to 800. The partially saponified polyvinyl alcohol having such a polymerization de-

gree may ultimately have an average polymerization degree in the aforesaid range as a whole and may contain partially saponified polyvinyl alcohols having a polymerization degree of less than 300 and/or more than 1,000 as the components. It is one of the excellent features of this invention that partially saponified polyvinyl alcohol having a polymerization degree over a wide range can be used as the component.

If the average polymerization degree of partially saponified polyvinyl alcohol after the preparation is less than 300, much scum forms in the emulsion, the emulsion is unstable because of phase separation, etc., and the viscosity of the emulsion is greatly reduced to make its workability poor upon application of the adhesive. On the other hand, if the average polymerization degree after the preparation is over 1,000, the viscosity of the emulsion is greatly increased to cause problems in industrial practice because the power required for stirring at the preparation of the emulsion is increased and, further, it becomes difficult to uniformly stir the emulsion.

The term "partial saponification" in the partially saponified polyvinyl alcohol in this invention means that the saponification degree is less than 96%. If the saponification degree is 96% or higher, the emulsion is accompanied by phase separation or precipitation to reduce the stability thereof. A preferred saponification degree is from 70% to less than 96%.

The content of such partially saponified polyvinyl alcohol in the vinyl acetate-ethylene copolymer emulsion is from 1.0 to 1.9 parts by weight, and preferably from 1.2 to 1.8 parts by weight per 100 parts by weight of the vinyl acetate unit. If the content of partially saponified polyvinyl alcohol is less than 1.0 part by weight, the emulsion is inferior in stability and the formation of scum from the emulsion is increased. On the other hand, if the content is over 1.9 parts by weight, the film formed from the emulsion is inferior in resistance to water blushing, wet strength and resistance to water retention.

One of the features of this invention resides in the finding that only when the content of partially saponified polyvinyl alcohol is in the specific range as described above, the copolymer emulsion shows an excellent effect in resistance to water blushing. In particular, the effect of improving the resistance to water blushing of the film of the emulsion is remarkable when the content of partially saponified polyvinyl alcohol is less than the aforesaid upper limit of the above range, and this effect is one of the excellent features of this invention.

The polyoxyethylene nonionic surface agent used in this invention has an HLB of from 16.5 to

17.5. If the HLB of the surface active agent is less than 16.5, the particle size of the emulsion becomes too large (the mean particle size thereof becomes larger than 0.90 μm), which results in reducing the initial adhesion properties of the emulsion. On the other hand, if the HLB is over 17.5, the emulsion particles formed during the polymerization reaction are ruptured to make the reaction system unstable, which results in undesirably forming a large amount of scum in the emulsion formed. The HLB as referred to herein is an index generally used for indicating the balance between hydrophilic groups and lipophilic groups in a surface active agent.

The content of such a polyoxyethylene nonionic surface active agent in the vinyl acetate-ethylene copolymer emulsion of this invention is from 1.0 to 3.0 parts by weight, and preferably from 1.5 to 2.8 parts by weight per 100 parts by weight of the vinyl acetate unit. If the content of the nonionic surface active agent is less than 1.0 part by weight, the emulsion is mainly inferior in low-temperature adhesion properties. On the other hand, if the content is over 3.0 parts by weight, the emulsion is inferior in resistance to thermal creep and resistance to water blushing as well as the reaction system at the polymerization becomes unstable and a large amount of scums is undesirably formed in the emulsion formed.

Specific examples of the polyoxyethylene nonionic surface active agent for use in this invention are polyoxyethylene alkyl ethers, polyoxyethylene alkyl-phenyl ethers, polyoxyethylene fatty acid esters and polyoxyethylene sorbitan fatty acid esters.

In the case of using the polyoxyethylene nonionic surface active agent having an HLB of from 16.5 to 17.5 in an amount defined in this invention, other polyoxyethylene nonionic surface active agents having an HLB falling outside the range defined in this invention may be used together in an amount of not more than 3.0 parts by weight per 100 parts by weight of the vinyl acetate unit and of not more than 35 parts by weight per 100 parts by weight of the polyoxyethylene nonionic surface active agent having an HLB of from 16.5 to 17.5.

The vinyl acetate-ethylene copolymer emulsion of this invention has an average particle size of not larger than 0.9 μm and a solids content of from 65 to 70% by weight. Since the copolymer emulsion of this invention has a high solids content, the emulsion shows excellent initial adhesion properties, which is one of the objects of this invention.

Now, the process for producing the vinyl acetate-ethylene copolymer emulsion is explained.

The process of this invention essentially comprises the following three steps.

The first step is a step of obtaining an aqueous solution containing 2.5 parts by weight or more but

less than 5.0 parts by weight of an emulsifying dispersant per 100 parts by weight of the whole of vinyl acetate to be polymerized by mixing with stirring from 1.0 to 1.9 parts by weight of partially saponified polyvinyl alcohol having an average polymerization degree of from 300 to 1,000 and from 1.0 to 3.0 parts by weight of a polyoxyethylene nonionic surface active agent having an HLB of from 16.5 to 17.5 per 100 parts by weight of the vinyl acetate together with a reducing agent of a redox catalyst, water, and, if desired, a pH buffer.

As the reducing agent of redox catalyst, which is used in the first step, reducing agents which are usually used for the production of vinyl acetate-ethylene copolymer emulsions can be used, and specific examples thereof are sodium (or zinc) formaldehyde sulfoxylate, sodium glyoxal hydrosulfite, and ferrous salts.

The whole amount of the reducing agent used may be added in this step. Alternatively, a part of the reducing agent is added in the step, and the residue may be added to the polymerization system in a third step described below.

The second step is a step of obtaining a stable vinyl acetate emulsified dispersion by adding from 40 to 90% by weight of the vinyl acetate to be polymerized to the aqueous solution of the emulsifying dispersant obtained in the first step, under stirring.

The stable vinyl acetate emulsified dispersion as referred to herein is an emulsified dispersion having such an extent of stability that when the dispersion is allowed to stand for from about 10 hours to 20 hours, vinyl acetate does not separate in the dispersion, and such a stable vinyl acetate emulsified dispersion is obtained by the second step as described above. On the other hand, when water, an emulsifying dispersant, and vinyl acetate are simultaneously added and mixed, vinyl acetate is added to an aqueous solution of an emulsifying dispersant without stirring, or a whole amount of vinyl acetate to be polymerized is added to an aqueous solution of an emulsifying dispersant at one time or under a similar condition with stirring, in place of employing the aforesaid step of this invention, a stable vinyl acetate emulsified dispersion cannot be obtained. Also, when such an unstable vinyl acetate emulsified dispersion is used, it becomes difficult to control the viscosity and particle size of the emulsion obtained in the subsequent polymerization step and the composition of the copolymer, whereby the quality of the emulsions obtained as the product is not uniform. Furthermore, in an extreme case, the viscosity of the emulsion becomes too high to allow the emulsion to be stirred during the polymerization.

The third step is a step of obtaining the vinyl

acetate-ethylene copolymer emulsion of this invention by carrying out a polymerization reaction at a polymerization temperature of from 30 to 80 °C and an ethylene pressure of from 10 to 100 kg/cm² by using the vinyl acetate-ethylene emulsified dispersion obtained in the second step, while adding successively from 10 to 60% by weight of vinyl acetate which is the residue of vinyl acetate to be polymerized, to the polymerization system during the polymerization and further adding thereto at least 0.004 mole of an oxidizing agent of a redox catalyst per kilogram of the whole of vinyl acetate supplied within 3 hours after the initiation of the polymerization.

In this invention, from 70 to 100% by weight of the emulsifying dispersant may be used in the first step and from 30 to 0% thereof (the residue) may be added to the polymerization system in the third step.

One of the features of this process resides in employing the separate addition system so that from 40 to 90% by weight, and preferably from 50 to 80% by weight of vinyl acetate to be polymerized is added in the second step and from 60 to 10% by weight, and preferably from 50 to 20% by weight thereof (the remaining vinyl acetate) is added in the third step.

When the amount of vinyl acetate added to the polymerization system in the third step is over the 50% ratio defined in this invention, an adhesive using the copolymer emulsion obtained is inferior in resistance to thermal creep. On the other hand, when the amount is less than the 20% ratio defined in this invention, the particle size of the emulsion becomes too large, the emulsion is inferior in initial adhesion properties, and the viscosity of the emulsion formed is increased to make it difficult to undergo stirring at the production of the emulsion.

Moreover, it is important in the polymerization reaction that the polymerization reaction rate at the beginning of the polymerization is kept high. If the polymerization reaction rate is not insufficient, the particle size of the emulsion becomes too large, and the initial adhesion properties of the emulsion become inferior. In this invention, for keeping the polymerization reaction rate high, a characteristic method of adding at least 0.004 mole of an oxidizing agent of a redox catalyst per kilogram of the whole of vinyl acetate supplied to the reaction system within 3 hours after the initiation of the polymerization reaction is employed. In addition, for keeping the reaction rate high at the beginning of the polymerization, it is useful to employ a lower temperature of initiating the polymerization reaction than ordinarily.

As the oxidizing agent of redox catalyst used in this invention, oxidizing agents which are usually used for the production of vinyl acetate-ethylene

copolymer emulsions can be used, and specific examples thereof are hydrogen peroxide, t-butyl peroxide, sodium persulfate, potassium persulfate, and ammonium persulfate. The amount of the oxidizing agent used in total in the process is usually from 0.05 to 0.15 part by weight per 100 parts by weight of vinyl acetate to be polymerized.

If the whole of the reducing agent to be used in the process is not added in the second step, the residue is added during the polymerization reaction in the third step.

The total amount of the reducing agent used in the second and third steps is in the range of from 0.5 to 1.5 moles per mole of the whole of the oxidizing agent.

In addition, a vinyl acetate-ethylene-third component copolymer may be used in place or together with the vinyl acetate-ethylene copolymer described above. The "third component" as referred to herein is a component having a functional group such as an amido group, a carboxylic acid group, a hydroxyl group, a sulfonic acid group, and an N-methylol group. Such a third component is contained in the range of not more than 10 parts by weight per 100 parts by weight of the vinyl acetate component.

The following examples are intended to illustrate this invention but not to limit it.

The evaluation methods (conditions) of emulsions employed in the following Examples and Comparison Examples are as follows.

1. Physical Properties of Emulsion:

(1) Solids content: Residue (weight %) after drying for 3 hours at 105 °C.

(2) Viscosity: BL-Type viscometer, 60 r.p.m., 25 °C.

(3) Mean particle size: The particle size was determined from the absorbance (wavelength of from 350 mμ to 600 mμ) of an emulsion diluted with water so as to have a solids content of 0.01% by weight.

Incidentally, a previously prepared particle size (by electron microscopic observation)-absorbance calibration curve was used.

(4) Scum: An emulsion was filtered by a wire gauze of 300 Tyler mesh, and the residue (weight %) on the wire gauze was defined as scum.

2. Resistance to Water Blushing of Film:

An emulsion was coated on a slide glass sheet and dried (23 °C, 65% RH) to form a film of 0.15 mm in thickness, the film was placed on Chinese characters of 8 point type of a newspaper, one water drop was dropped on the film, and the time

required until the characters became unreadable through the film by blushing of the film was measured. As the time is longer, the resistance to water blushing is higher.

3. Adhesion Performance:

(1) Initial adhesion properties: A corrugated board (basis weight 200 g/m²) was coated with 3 ml (wet) of an emulsion, a wood-free paper (basis weight 90 g/m²) was superposed on the emulsion-coated layer, and after pressing them by rubber rollers, the time required until the paper caused 100% break at 23°C, 65% RH was measured. As the time is shorter, the initial adhesion properties are better.

(2) Cloth/cloth adhesion properties: A piece of No 40 cotton broad cloth was coated with an emulsion (100 g/m²), another piece of the broad cloth was superposed thereon, and after pressing them at 0.01 kg/cm² for 18 hours, the assembly was cured for 6 days at 23°C, 65% RH. Thereafter, the following properties were measured.

(a) Dry strength: The strength of the assembly by T-form peeling a one inch (2.54 cm) width was measured.

(b) Wet strength: The strength of the assembly after being immersed in water for one hour was measured.

(c) Resistance to thermal creep: A load of 500 g was hung down from the assembly in a one inch (2.54 cm) width, and the peeled length after allowing to stand at 80°C for one hour was measured. As the length is shorter, the resistance to thermal creep is higher.

(d) Resistance to water retention: A value of (wet strength/dry strength) × 100 was employed as the resistance to water retention. As the value is nearer 100, the resistance to water retention is higher.

(3) Cloth/plastic adhesion properties: A piece of No 40 cotton broad cloth was coated with an emulsion (100 g/m²), a plastics film (PET or OPP) was superposed thereon, and after pressing them by rubber rollers, the assembly was cured for 4 days at 23°C, 65% RH. Thereafter, the following properties were measured.

(a) Dry strength: A strength of the assembly by peeling at 180 degree in one inch width was measured.

(b) Wet strength and resistance to water retention: Same as the aforesaid measurement methods for the cloth/cloth adhesion properties.

(4) Polyvinyl chloride/plywood adhesion properties: A lauan plywood (JAS Class 1, 1st grade, 3 mm thick) was coated with an emulsion (150 g/m²), a polyvinyl chloride sheet (semi-rigid

doubling sheet) was laminated thereon, and after pressing them for 20 days at 0.05 kg/cm², the assembly was cured for 6 days at 23°C, 65% RH. Thereafter, the following properties were measured.

(a) Dry strength: Same as the aforesaid measurement method for the cloth/plastic adhesion properties.

(b) Low-temperature adhesion properties: A test piece of the assembly was cut into a 1 cm width, was allowed to stand for 20 hours at -20°C, the polyvinyl chloride sheet was quickly peeled from the cloth by hand, and the degree of breakage of the wood was measured. As the value is larger, the low-temperature adhesion properties are better.

EXAMPLE 1

(a) In a 300-liter pressure-resisting reaction vessel equipped with a stirrer were placed 49,200 ml of water, 260 ml of 50 wt% acetic acid (pH buffer solution), 1,340 g of partially saponified polyvinyl alcohol having a polymerization degree of 350 and a saponification degree of 89%, 1,340 g of partially saponified polyvinyl alcohol having a polymerization degree of 550 and a saponification degree of 89% (average polymerization degree of two kinds of partially saponified polyvinyl alcohol: 450, ratio of the polyvinyl alcohols to the total amount of vinyl acetate: 1.8/100 by weight), and 2,235 g of polyoxyethylene nonylphenyl ether having an HLB of 17.1 (ratio to the total amount of vinyl acetate: 1.5/100 by weight), followed by stirring for 60 minutes at 30°C and 230 r.p.m. to provide a uniform aqueous solution. Then, 2 g of ferrous sulfate and 5,200 ml of a 7 wt% sodium formaldehyde sulfoxylate aqueous solution were added to the uniform aqueous solution as reducing agents of a redox catalyst to provide an aqueous solution of an emulsifying dispersant.

(b) Then, to the aqueous solution of emulsifying dispersant was added 104 kg in total of vinyl acetate (70% by weight of the total amount of vinyl acetate) at an addition rate of 112 kg/hour under stirring at 230 r.p.m. to provide a vinyl acetate emulsified dispersion. The dispersion obtained was so stable that neither phase separation nor precipitation occurred when the dispersion was allowed to stand overnight.

(c) Then, while stirring the vinyl acetate emulsified dispersion at 230 r.p.m., the atmosphere in the reaction vessel was replaced with nitrogen and then with ethylene, the ethylene pressure in the reaction vessel was increased while increasing the temperature, and when the temperature and pressure reached 60°C and 45 kg/cm², respectively, a 0.30 wt% hydrogen peroxide aqueous solution (an

oxidizing agent of a redox catalyst) was added to the dispersion at a rate of 3.80 liters/hour for 6.5 hours, and at the same time, the remaining 45 kg of vinyl acetate was added thereto at a rate of 7.5 kg/hour. The hydrogen peroxide was added in an amount of 0.008 mole per kilogram of the whole of the vinyl acetate supplied a time until 3 hours after the initiation of the polymerization reaction.

During the aforesaid addition operation, the system was kept at 60°C and an ethylene pressure of 45 kg/cm².

When the proportion of unreacted vinyl acetate became 1% by weight or less of the whole of vinyl acetate supplied, the reaction was defined to be finished.

The emulsion obtained was evaluated by the methods described above, and the results are shown in Table 1 below, with those of other Examples and Comparison Examples.

EXAMPLE 2

The same procedures as in Example 1 were followed, except that 1,900 g (ratio to the total amount of vinyl acetate: 1.3/100 by weight) of only one partially saponified polyvinyl alcohol having a polymerization degree of 550 and a saponification degree of 89% was used as the partially saponified polyvinyl alcohol.

EXAMPLE 3

The same procedures as in Example 1 were followed, except that two types of polyoxyethylene nonylphenyl ether were used, namely 2,235 g having an HLB of 17.1 and 745 g having an HLB of 31.2 (ratio of both surfactants to the total amount of vinyl acetate: 1.5/100 by weight) were used together as the polyoxyethylene surface active agent.

EXAMPLE 4

Example 1 was repeated except that

(a) the partially saponified PVA was added in amount of 1940 g of polymerisation degree 89% with 600 g of one of polymerization degree of 1050 (average polymerization degree 515, ratio of the PVAs to total vinyl acetate 1.7/100), and there was added further a polyoxyethylene nonylphenyl ether of HLB 13.2 in amount of 745 g (ratio thereof to total vinyl acetate: 0.5/100),

(b) the vinyl acetate amount added was 75

kg (50% of the total) at a rate of 80 kg/hour, and

(c) the hydrogen peroxide aqueous solution addition rate was 4.55 liters/hour for 5.5 hours, and the remaining vinyl acetate was added in amount of 74 kg at a rate of 15 kg/hour, the hydrogen peroxide addition being in amount of 0.01 mole per kg of the total vinyl acetate.

EXAMPLE 5

The same procedures as in Example 4 were followed, except that 1,490 g (ratio to the total amount of vinyl acetate: 1.0/100 by weight) of partially saponified PVA having a polymerization degree of 350 and a saponification degree of 89% and 1,190 g (ratio to the total amount of vinyl acetate: 0.8/100 by weight) were used as the partially saponified polyvinyl alcohol.

COMPARISON EXAMPLE 1

The same procedures as in Example 1 were followed, except that 600 g of partially saponified polyvinyl alcohol having a polymerization degree of 350 and a saponification degree of 89% and 600 g of partially saponified polyvinyl alcohol having a polymerization degree of 550 and a saponification degree of 89% were used as the partially saponified polyvinyl alcohol.

In this comparison example, the amount of partially saponified polyvinyl alcohols (ratio to the total amount of vinyl acetate: 0.8/100 by weight) was less than the amount defined in this invention, and the emulsion was accompanied by the formation of scum in amount of 50,000 ppm, which was outside the limit for practical use.

COMPARISON EXAMPLES 2 AND 3

The same procedures as in Example 1 were followed, except that 1,520 g of partially saponified polyvinyl alcohol having a polymerization degree of 350 and a saponification degree of 89% and 1,520 g of partially saponified polyvinyl alcohol having a polymerization degree of 550 and a saponification degree of 89% (Comparison Example 2) or 2,235 g of partially saponified polyvinyl alcohol having a polymerization degree of 350 and a saponification degree of 89% and 2,235 g of partially saponified polyvinyl alcohol having a polymerization degree of 550 and a saponification degree of 89% (Comparison Example 3) were used as the partially

saponified polyvinyl alcohol.

In these comparison examples, the amount of the partially saponified polyvinyl alcohols (ratio to the total amount of vinyl acetate: 2.0/100 by weight in Comparison Example 2 and 3.0/100 by weight in Comparison Example 3, respectively) was larger than the amount defined in this invention, and the emulsions obtained were inferior, in particular, in resistance to water blushing, wet strength and resistance to water retention of film.

COMPARISON EXAMPLE 4

The same procedures as in Example 1 were followed, except that 1,680 g of partially saponified polyvinyl alcohol having a polymerization degree of 250 and a saponification degree of 89% was used as the partially saponified polyvinyl alcohol.

In this comparison example, the polymerization degree (250) of partially saponified polyvinyl alcohol was less than that defined in this invention, and the emulsion formed was accompanied by the formation of about 2,000 ppm of scums as well as a supernatant liquid was formed during allowing to stand the emulsion, which were outside the evaluation for practical use.

COMPARISON EXAMPLE 5

The same procedures as in Example 1 were followed, except that 1,680 g of partially saponified polyvinyl alcohol having a polymerization degree of 1,150 and a saponification degree of 89% was used as the partially saponified polyvinyl alcohol.

In this comparison example, the polymerization degree (1,150) of partially saponified polyvinyl alcohol was larger than that defined in this invention, whereby the viscosity of the emulsion was greatly increased during the polymerization to make the stirring operation difficult. Furthermore, the emulsion formed has a solids content of 66.7% by weight and a viscosity of 10,000 cps or more, which were outside the evaluation for practical use.

COMPARISON EXAMPLE 6

The same procedures as in Example 1 were followed, except that 2,235 g polyoxyethylene nonylphenyl ether having an HLB of 15.7 was used as the polyoxyethylene nonionic surface active agent.

In this comparison example, the HLB of the polyoxyethylene nonionic surface active agent used

was smaller than that defined in this invention. Thus, the mean particle size of the emulsion obtained became too large, a large amount of scum was formed, and in particular, the emulsion was inferior in initial adhesion properties.

COMPARISON EXAMPLE 7

The same procedures as in Example 1 were followed, except that 1,192 g polyoxyethylene nonylphenyl ether having an HLB of 17.1 was used as the polyoxyethylene nonionic surface active agent.

In this comparison example, the amount (ratio to the total amount of vinyl acetate: 0.8/100 by weight) of the polyoxyethylene nonionic surface active agent was less than that defined in this invention, and the emulsion obtained was accompanied by the formation of a large amount of scums and was inferior in initial adhesion properties and low-temperature adhesion properties in the polyvinyl chloride/plywood adhesion properties.

COMPARISON EXAMPLE 8

The same procedures as in Example 1 were followed, except that 5,215 g polyoxyethylene nonylphenyl ether having an HLB of 17.1 was used as the polyoxyethylene nonionic surface active agent.

In this comparison example, the amount (ratio to the total amount of vinyl acetate: 3.5/100 by weight) of the polyoxyethylene nonionic surface active agent was too larger than that defined in this invention, and the emulsion obtained was accompanied by the formation of a large amount of scums and was inferior in, in particular, resistance to thermal creep, wet strength, and resistance to water retention.

COMPARISON EXAMPLE 9

The same procedures as in Example 1 were followed, except that the whole (149 g) of vinyl acetate to used was added one time to the aqueous solution of emulsifying dispersant.

The emulsion obtained without employing the separate addition system of vinyl acetate, which was a feature of this invention, had too large a mean particle size and unusually high viscosity and was inferior in initial adhesion properties.

COMPARISON EXAMPLE 10

The same procedures as in Example 1 were followed, except that 37 kg of vinyl acetate was added to the aqueous solution of emulsifying dispersant and that 112 kg of vinyl acetate was then added thereto at a rate of 79 kg/hour during the polymerization reaction.

In this comparison example, the amount of vinyl acetate initially added to the aqueous solution of emulsifying dispersant (25% of the total amount of vinyl acetate used) was less than that defined in this invention, and the emulsion obtained was accompanied by the formation of a large amount of scums and was inferior in resistance to thermal creep.

COMPARISON EXAMPLE 11

The same procedures as in Example 1 were followed, except that 104 kg of vinyl acetate was added to the aqueous solution of emulsifying dispersant over a period of 10 minutes. The vinyl acetate emulsified dispersion obtained was unstable so that phase separation occurred after 3 hours, and when polymerization reaction was carried out using such an unstable vinyl acetate emulsified dispersion, the viscosity of the reaction system was abnormally increased after 3 hours since the initiation of polymerization so that it became impossible to further continue the polymerization reaction.

COMPARISON EXAMPLE 12

The same procedures as in Example 1 were followed, except that a 0.15 wt% hydrogen peroxide aqueous solution was added at a rate of 2.85 liters/hour for 8.5 hours.

In this comparison example, the amount of the oxidizing agent supplied within 3 hours since the initiation of the polymerization reaction was 0.003 mole per kilogram of the total amount of vinyl acetate supplied until that time, which was too less than that defined in this invention, and the emulsion had too large a mean particle size and high viscosity and was inferior in initial adhesion properties.

Table 1

	Example					Comparison Example							
	1	2	3	4	5	2	3	6	7	8	9	10	12
Properties of Emulsion													
Solids Content (wt%)	67.2	67.0	68.0	66.9	67.1	67.0	66.6	67.4	67.4	67.6	67.2	67.7	67.0
Viscosity (cps)	1300	2000	1500	2200	3900	1520	1760	1000	1300	1970	7700	800	3500
Mean Particle size (μm)	0.76	0.78	0.74	0.74	0.76	0.77	0.78	1.01	0.86	0.70	1.12	0.69	1.03
Scums (ppm)	87	90	40	34	70	55	70	128	580	1320	25	700	30
Ethylene Content (wt%)	19.0	19.1	19.6	18.9	19.2	19.0	18.2	18.9	18.8	18.4	18.3	18.8	19.2
Resistance of Water Blushing of Film (min)	>120	>120	>120	>120	>120	60	15	>120	>120	80	>120	>120	105

Table 1 (continued)

	Example					Comparison Example							
	1	2	3	4	5	2	3	6	7	8	9	10	12
Adhesion Performance													
Initial Adhesion Properties (min.)	10	10	8	8	10	10	10	32	16	10	40	8	38
Cloth/cloth Adhesion Properties													
Resistance to Thermal Creep (mm/hr)	18	15	20	20	20	20	20	18	18	140	20	130	20
Dry Strength (kg/in)	4.5	4.6	4.4	4.6	4.5	4.5	4.6	4.4	4.5	4.6	4.5	4.4	4.5
Wet Strength (kg/in)	2.4	2.5	2.3	7.4	2.4	1.4	1.2	2.2	2.3	1.8	2.3	2.2	2.3
Resistance to Water Retention (%)	53	54	52	52	53	31	26	50	51	39	51	50	51

Table 1 (continued)

	Example					Comparison Example							
	1	2	3	4	5	2	3	6	7	8	9	10	12
Adhesion Performance													
Cloth/Plastic Adhesion Properties													
Cloth/PET													
Dry Strength (kg/in)	490	470	500	490	480	480	430	480	500	470	480	470	460
Wet Strength (kg/in)	390	380	410	400	380	240	200	360	400	240	380	380	370
Resistance to Water Retention (%)	80	81	82	82	79	50	47	75	80	51	79	81	80
Cloth/OPP													
Dry Strength (kg/in)	320	310	320	310	310	300	260	310	300	310	310	320	300
Wet Strength (kg/in)	200	190	200	200	190	160	130	190	180	170	190	200	180
Resistance to Water Retention (%)	63	61	63	65	61	53	50	61	60	55	61	63	60

Table 1 (continued)

Example					Comparison Example							
1	2	3	4	5	2	3	6	7	8	9	10	12

Adhesion Performance

Polyvinyl Chloride/
Plywood Adhesion Properties

Dry Strength (kg/in) 4.5 4.5 4.5 4.5 4.5 4.4 4.3 4.5 4.4 4.5 4.5

Low-Temperature Adhesion Properties good good good good good poor good good good good good

Note: Resistance to Water Retention = (Dry Strength/Wet Strength) × 100 (%)

As described above, the invention can provide a vinyl acetate-ethylene copolymer emulsion capable of providing an adhesive which is excellent mainly in all the points of initial adhesion properties, resistance to thermal creep, low-temperature adhesion properties, dry strength and wet strength, resistance to water retention, and resistance to water blushing and can be suitably used for various materials to be adhered and also can provide a production process of the vinyl acetate-ethylene copolymer emulsion without being accompanied by the formation of scums and industrially advantageously owing to a proper viscosity of the emulsion.

The emulsions of the invention are actually aqueous dispersions of particles of the copolymer, which floats in water; such dispersions are conventionally referred to in the art as "emulsions".

Claims

1. An aqueous emulsion of a copolymer of acetate and ethylene composed of from 10 to 40% by weight of an ethylene unit and from 90 to 60% by weight of a vinyl acetate unit and an emulsifying dispersant in an amount of from 2.5 parts by weight or more but less than 5.0 parts by weight per 100 parts by weight of the vinyl acetate unit, and having a mean particle size of not larger than 0.9 μm and a solids content of from 65 to 75% by weight;

wherein the emulsifying dispersant contains (i) from 1.0 to 1.9 parts by weight of partially saponified polyvinyl alcohol prepared so as to have an average polymerization degree of from 300 to 1,000 and (ii) from 1.0 to 3.0 parts by weight of a polyoxyethylene nonionic surface active agent having a hydrophilic-lipophilic balance of from 16.5 to 17.5, each per 100 parts by weight of the vinyl acetate unit.

2. A copolymer emulsion as claimed in Claim 1, wherein the content of said partially saponified polyvinyl alcohol (i) is from 1.2 to 1.8 parts by weight per 100 parts by weight of the vinyl acetate unit.

3. A copolymer emulsion as claimed in Claim 1 or 2, wherein said partially saponified polyvinyl alcohol (i) contains as a component partially saponified polyvinyl alcohol having a polymerization degree of over 1,000 and/or partially saponified polyvinyl alcohol having a polymerization degree of less than 300.

4. A copolymer emulsion as claimed in Claim 1, 2 or 3, wherein the content of said surface active agent (ii) is from 1.5 to 2.8 parts by weight.

5. A process for producing a vinyl acetate-

ethylene copolymer emulsion as claimed in Claim 1, 2, 3 or 4, said process comprising:

a first step of mixing with stirring from 1.0 to 1.9 parts by weight of partially saponified polyvinyl alcohol prepared so as to have an average polymerization degree of from 300 to 1,000 and from 1.0 to 3.0 parts by weight of a polyoxyethylene nonionic surface active agent having an HLB of from 16.5 to 17.5 per 100 parts by weight of the whole of vinyl acetate to be polymerized together with a reducing agent of a redox catalyst, water, and optionally, a pH buffer to provide an aqueous solution containing from 2.5 parts by weight or more but less than 5.0 parts by weight of the emulsifying dispersant per 100 parts by weight of the vinyl acetate;

a second step of adding from 40 to 90% by weight of the vinyl acetate to be polymerized to the aqueous solution of the emulsifying dispersant under stirring to provide a stable vinyl acetate emulsified dispersion; and

a third step of carrying out a polymerization reaction at a polymerization temperature of from 30 to 80°C and an ethylene pressure of from 98 to 980 Pa (10 to 100 kg/cm²) by using the vinyl acetate emulsified dispersion, while successively adding the remaining 10 to 60% of the vinyl acetate to be polymerized to the polymerization system during the polymerization and further adding thereto at least 0.004 mole of an oxidizing agent of redox catalyst per kilogram of the whole of vinyl acetate supplied within 3 hours after the initiation of the polymerization.

6. An emulsion or process as claimed in any preceding claim, wherein the copolymer includes up to 10 parts by weight, per 100 parts of the vinyl acetate component, of a third component having a functional group.